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Fabrication of High Temperature Thermoelectric Energy Harvesters for Wireless Sensors

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Abstract.

Implementing energy harvesters and wireless sensors in jet engines could simplify development and decrease costs. A thermoelectric energy harvester could be placed in the cooling channels where the temperature is between 500-900 $^{\circ}$ C. This paper covers the synthesis of suitable materials and the design and fabrication of a thermoelectric module. The material choices and other design variables were done from an analytic model by numerical analysis. The module was optimized for $600-800^{\circ}$ C with the materials $Ba_8Ga_{16}Ge_{30}$ and La-doped $Yb_{14}MnSb_{11}$, both having the highest measured zT value in this region. The design goal was to be able to maintain a temperature gradient of at least 200°C with high power output. The La-doped Yb₁₄MnSb₁₁ was synthesized and its structure confirmed by x-ray diffraction. Measurement of properties of this material was not possible due to insufficient size of the crystals. $Ba_8Ga_{16}Ge_{30}$ was synthesized and resulted in an approximated zT value of 0.83 at 700° C. Calculations based on a module with 17 couples gave a power output of 1100 mW/g or $600 \mathrm{mW/cm^2}$ with a temperature gradient of 200K.

1. Introduction

Measuring pressure, temperature, stress and acceleration is essential for safe operation of jet engines. For test engines in development this means thousands of sensors and kilometers of wire connecting the sensors. In the middle and the back of the jet engine it is more complicated to place sensors due to both high temperature and the need for extensive cable wiring. Cable wiring and the cost and weight of copper wire is a problem but can be reduced by replacing the wired sensors with wireless sensors coupled with energy harvesters as power sources.

In the hot parts of the jet engine the walls are cooled down with air through cooling channels. Placing thermoelectric energy harvesters inside the cooling channels would give a hot side of $800-900^{\circ}$ C at the wall with cooling air of $500-600^{\circ}$ C on the cold side. This means that the thermoelectric module could have a temperature gradient of 200°C if the heat transfer through the module is low enough.

This paper is a summary of an ongoing attempt to design and fabricate a small thermoelectric module optimized for the temperature range of 600-800°C with high power output rather than high efficiency, and with capability to withstand a temperature gradient of 200°C.

2. Design

To optimize the design for the temperature range and the environment an analytic model was constructed. The model included heat input, heat output, Joule heating, heat conduction [1], heat transfer in base plates, parasitic thermal conductivity [2] and contact resistance [3], the model also included load resistance matching, the resistance of cables and DC-DC conversion losses when connected to a voltage step up booster circuit. The step up booster is used to increase the voltage to an appropriate level to power the sensors, in this case 3.3V.

The choice of materials and variables such as number of couples in square devices, height of thermoelectric legs, area of legs, area ratio between n-type and p-type material, thickness of electrodes (resistance of contacts), load resistance, base plates material, electrode material and material between couples (parasitic conductance) was done by numerical analysis of the model. These materials and variables were chosen to give the highest power output possible when connected to a DC/DC converter circuit. The thermoelectric materials was chosen based on simulations, and the best results came from n-type $Ba_8Ga_{16}Ge_{30}$ [4] and p-type La-doped $Yb_{14}MnSb_{11}$ [5], both with measured figure of merit above 1.2 in the temperature range. These materials also have similar thermal expansion, with $14.2\mu m/K$ [6] and $17.5\mu m/K$ [7] respectively.

3. Synthesis

 $Ba_8Ga_{16}Ge_{30}$ was synthesized by heating barium, gallium and germanium with an 2.5% excess of barium to 1050°C to ensure melting before cooled to 963°C were it was held for 38h and then cooled at -100°C/h to room temperature. This synthesis method has been shown to produce good results [8]. The result was 20g of large $Ba_8Ga_{16}Ge_{30}$ single crystals with sizes up to 1cm in length, see fig. 1. The synthesis of La-doped Yb₁₄MnSb₁₁ followed a recipe [5] using a tin flux with an Yb:La:Mn:Sb:Sn-ratio of 13:1:6:11:86. The crystals from this synthesis were smaller than the $Ba_8Ga_{16}Ge_{30}$ crystals and had tin impurities remaining on the crystals, see fig. 2.



Figure 1. 20g of $Ba_8Ga_{16}Ge_{30}$ single crystals. The size of the crystals was relatively consistent with some having a length of 1 cm making measurement of Seebeck coefficient and resistivity possible.



Figure 2. La-doped $Yb_{14}MnSb_{11}$ crystals covered in a thin film of Sn. No crystals were big enough to enable measurement of Seebeck coefficient, electrical resistivity or thermal conductivity.

4. Fabrication

The module was built with alumina base plates which were cut into a size of 1cm^2 . Because Ladoped $Yb_{14}MnSb_{11}$ reacts with most materials but is known to be stable with graphite, alumina

and molybdenum [9] the choice of electrode material was molybdenum. 80μ m thick electrodes were glued on to the base plates with high temperature ceramic glue. The thermoelectric legs were cut with a diamond saw and placed in a grid of alumina paste which has been seen to suppress sublimation of Yb₁₄MnSb₁₁ [10]. The grid also stabilized the module and kept the thermoelectric legs in place during the fabrication process, see fig 3.



Figure 3. A grid is made out of an alumina paste and placed on the base plates. The thermoelectric materials is placed in a grid which keeps the legs in place and stabilizes the module when the top base plate has been placed.

To ensure connection between the electrodes and the thermoelectric materials the electrodes were shaped as springs. Also, a thin layer of graphite was placed between the electrodes and thermoelectric legs to improve the connection further. The force needed to get a good connection through the device was quite high and a large weight or a vise was necessary for low contact resistance. Sealing the device was done with alumina paste and two different types of ceramic glues and was done to keep oxygen away from the thermoelectric materials and the electrodes.

5. Results

5.1. Simulation

The module design was, based on the analytic model, optimized for maximum power output with a temperature gradient of 200°C. Highest power output was given with 17-couples, 1mm leg height and the optimal n-type:p-type area ratio of 0.27:0.73. Simulation of power output, voltage and efficiency based on these values gave a power output of 750mW, voltage of 640mV and an efficiency of 3.3% with a 200°C temperature gradient of the environment, see fig. 4.



Figure 4. Estimated power output (blue line) and voltage (green, dashed line) as a function of the temperature gradient of the environment. No DC/DC converter circuit is connected in this simulation.

When including losses from cables and a low voltage DC/DC converter with a load resistance of 2.5Ω the power output is decreased to 123mW with a voltage of 1060mV. In this simulation the conversion efficiency in the step up converter was 30%.



Figure 5. Estimated power output (blue line) and voltage (green, dashed line) as a function of the load resistance. The calculations are based on 2m long high temperature cables commonly used in jet engines with a wire resistance of $0.16\Omega/m$ and a low voltage step up converter with 30% efficiency.

5.2. Synthesis

The synthesis of $Yb_{14}MnSb_{11}$ resulted in crystals that were too small to do any measurements of Seebeck coefficient, resistivity or thermal conductivity. The material was identified by x-ray diffraction measurements. The synthesis of $Ba_8Ga_{16}Ge_{30}$ gave single crystals large enough to measure Seebeck coefficient and resistivity but not thermal conductivity. The measurement was done from room temperature to 725°C and back to room temperature and showed negligible hysteresis between the heat up and the cool down measurement. The measured Seebeck coefficient and resistivity during the cool down can be seen in fig. 6 and 7.



Figure 6. Seebeck coefficient measurement on $Ba_8Ga_{16}Ge_{30}$. The measurement was done from 725°C to room temperature. No hysteresis could be seen between heat up and cool down.



Figure 7. Resistivity measurement on $Ba_8Ga_{16}Ge_{30}$. Measured between 725°C and room temperature while cooling down.



Figure 8. Approximated figure of merit of $Ba_8Ga_{16}Ge_{30}$, based on typical thermal conductivity [4] values from single crystals and the measured Seebeck coefficient and resistivity from this synthesis.

With no measurement of thermal conductivity the figure of merit of $Ba_8Ga_{16}Ge_{30}$ could not be calculated. However, the difference in thermal conductivity for single crystal $Ba_8Ga_{16}Ge_{30}$ is small between different syntheses, and an approximation based on known thermal conductivity results [4] was done. The approximation shows a figure of merit of 0.7-0.83 in the temperature range 600-725°C, see fig. 8.

6. Discussion and conclusion

To power a wireless sensor with a thermoelectric energy harvester the voltage should be stable and in the region of 2.5-3.5V. The simulations when connected to a DC/DC converter circuit shows a huge decrease in power output, mainly because of the poor conversion efficiency from the low voltage and from the poor load resistance matching. This problem can be improved by connecting several thermoelectric modules in series to increased the voltage to make it possible to use more efficient DC/DC converters. Simulations with 4 modules in series give a power output of approximately 2W with 3.3V output with 200°C temperature gradient. As most sensors require only a few mW of power, this energy harvester solution would give enough power for a large sensor network.

The approximated figure of merit of 0.83 at 700°C for $Ba_8Ga_{16}Ge_{30}$ is higher than what other common thermoelectric materials can achieve at this temperature. When coupled with La-doped Yb₁₄MnSb₁₁ these materials could prove to be a powerful combination in the temperature range of 600-800°C. The successful synthesis of the n-type material and the steps so far tested, shows promise for the complete assembly of a functional high temperature thermal harvester.

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